### EMERGING APPLICATIONS OF HYDROGEN IN CLEAN TRANSPORTATION

Venki Raman Air Products and Chemicals Inc. Allentown, PA 18195

Key Words: Hydrogen, Hythane®, Hydrogen vehicles

#### Introduction

The present total dependence on oil supplies for our transportation systems is the major cause of air pollution in the growing urban areas of the world, and is clearly unsustainable into the future. The societal will to seek changes in this system is evidenced by the passage of stringent clean air standards that require clean alternative fuels. Emerging trends suggest that we will gradually move from this oil-dependent system to a transportation system that favors cleaner fuels such as natural gas in the near term. For the longer term, our aim will be to use pollution-free fuels derived from renewable resources. At the same time, there will also be a shift from the rather inefficient internal combustion (IC) engine that has dominated our automotive systems to highly efficient, electric motors. The combination of new fuels and new engines to use them, will ultimately produce a new transportation system built entirely on sustainable energy.

Because hydrogen can be produced cleanly from renewable energy resources, and used virtually without any pollution, it may prove to be the ideal energy carrier in the future automobile systems. A plausible strategy for the transition to hydrogen, that is widely subscribed to in the international hydrogen energy community, could involve the initial replacement of present day gasoline and diesel with natural gas, followed by the gradual introduction of hydrogen, which is similar to natural gas in the practical aspects of distribution, transfer and storage.

The key feature of past energy transitions has been the progressive move toward fuels containing less carbon and more hydrogen; witness the shift from dried wood which is mostly carbon (10% hydrogen), to coal (38% hydrogen), oil (64% hydrogen), and natural gas (80% hydrogen). The transition to hydrogen merely continues this pattern. The energy content of the fuels increases as the percentage of hydrogen increases. The shift to fuels containing less carbon has lessened air pollution over the past century (per pound burned). Particulates and carbon dioxide from oil burning are significantly lower than that from burning coal to release the same amount of energy. The shift to natural gas will cut this further and with hydrogen totally eliminated.

## **International Hydrogen Activities**

Driven by concerns about oil dependence, and air quality, and recognizing the benefits of a hydrogen-based transportation energy system, over 30 countries worldwide, have active R&D programs underway in hydrogen energy applications. Major programs are being undertaken in Japan, the U.S. and Germany. Except for space applications which the U.S. leads, the leadership in hydrogen R&D centers in Japan and Germany. Japan has the most ambitious hydrogen energy R&D program called World Energy Network (WE-NET) which is a \$2 billion effort over twenty-eight years (1993-2020). Germany has been the leader in hydrogen vehicle applications, and second to Japan in total spending on hydrogen R&D. The U.S. comes in third, followed by Canada, where the province of Quebec has undertaken a major program aimed at looking at harnessing its vast hydroelectric power resources to make liquid hydrogen for export to Europe.

In Germany, the birthplace of the automobile, Daimler-Benz and BMW have pioneered the development of hydrogen-fueled vehicles for over two decades. Daimler-Benz has developed hydrogen IC engines for cars and vans, using metal hydrides for onboard storage of hydrogen, and operated fleets of vehicles in Berlin. More recently their efforts have shifted to buses with liquid hydrogen stored onboard. Several buses are being built in conjunction with bus manufacturer MAN for operation in urban transit, and airport shuttle bus service. A joint German - Russian team including Daimler-Benz Aerospace and Tupolev are in early stages of development of a liquid hydrogen airplane called "Cryoplane". Perhaps the most exciting development at Daimler-Benz has been their unveiling in May 1996 of their second generation hydrogen fuel cell passenger minivan called "NECAR 2" with hydrogen stored onboard as compressed gas. The first prototype NECAR 1 a research vehicle had been unveiled only in 1994. This development program is clearly proceeding at an accelerated pace at Daimler-Benz. The next prototype NECAR 3 is expected to be a new small sedan.

BMW has also been active in hydrogen car developments since about 1979. The focus of BMW's efforts have been centered on liquid hydrogen from the start. BMW has developed 6 generations of cars capable of running on either gasoline or hydrogen. In conjunction with German hydrogen suppliers, they have significantly improved the insulating efficiency, and compactness of onboard liquid hydrogen storage tanks. They have also reduced fueling times from about 1 hour down to about 15 minutes. Now they are developing robotic fueling systems to fully automate the transfer of liquid hydrogen to the car. BMW also participates in a consortium that is conducting a solar-hydrogen demonstration project in Germany.

This facility is an integrated project that produces hydrogen via water electrolysis from solar generated electricity.

In Japan, active hydrogen vehicle projects are underway at Mazda, Toyota, Honda, and Musashi Institute of Technology. Mazda's work has been on hydrogen-fueled IC rotary engines using metal hydrides to store hydrogen onboard the vehicle. Toyota unveiled their first hydrogen fuel cell car in October 1996.

The U.S. Department of Energy has been researching the potential use of hydrogen as an energy carrier and fuel since the early 1970s, following the OPEC oil embargo. Originally, the driving force behind this program was the National need to develop a domestic, sustainable energy base. Basic R&D was conducted at a low level of funding (\$0.5-1.0 million) throughout the 1980s. However in 1990 the U.S. Congress enacted into law the Spark Matsunaga Hydrogen Research, Development, and Demonstration Act (P.L. 101-566) which revitalized the then existing Hydrogen Program. The Energy Policy Act of 1992 (P.L.102-486) further supplemented the Matsunaga Act. These actions have resulted in a National Hydrogen R&D program under the management of the DOE which has a current budget of \$15 million per year. A new Hydrogen Futures Act of 1996 (P.L. 104-271) was recently enacted authorizing expenditures of \$150 million between 1997 and 2001 for hydrogen R&D and demonstration programs. In addition to the Hydrogen Program, DOE supports other hydrogen related programs including work on fuel cell technologies to the tune of \$100 million per year.

In addition to the federal program, several state and regional government bodies have also initiated hydrogen vehicle programs of their own including the South Coast Air Quality Management District (SCAQMD) in Southern California, the California Air Resources Board (CARB), Cities of Palm Desert, Palm Springs, and Denver, New York State Energy Research and Development Authority (NYSERDA), Pennsylvania Energy Office (PEO), and others.

j

### **Hydrogen Transportation Demonstration Programs**

In the area of hydrogen vehicles, active programs are underway in IC engines, IC engine-electric hybrids, and fuel cell engines. These programs represent a progression of increasingly more economically and technically challenging options for the transition of hydrogen into the transportation fuel marketplace.

## Hythane®

From the earliest days of combustion science, experiments have established that hydrogen has a strong influence on the combustion of natural gas and other hydrocarbons. More recently, Hydrogen Components Inc., of Colorado has been actively promoting the use of dilute concentrations of hydrogen (10-20 Vol%) blended with natural gas in IC engines. They have registered the trademark Hythane, and hold a patent on the application of Hythane in IC engines.

It has been shown in laboratory and on-the-road testing that this small level of hydrogen addition to natural gas in IC engines results in reducing levels of carbon monoxide (CO) and oxides of nitrogen (NOx) emissions from these engines an additional 50% over that achieved with "straight" natural gas. The economic rationale for such an approach involving small additions of expensive hydrogen to cheap natural gas relates to the fact that significant leverage in emissions reduction is achieved, i.e., disproportionately greater than the amount of hydrogen added. Such an approach faces a smaller economic hurdle in achieving the benefits of clean air and is more likely to be favorably received by the consumer.

The Hythane application has been developed and tested for gasoline (stoichiometric engines) and diesel type (lean burn) engines1. Several test and demonstration programs have been conducted in Denver, Colorado, Erie, Pennsylvania, and Montreal, Canada on small fleets of utility service vehicles and urban transit buses. In these programs optimal hydrogen additions were determined to be between 15-20 vol%. In the case of buses operating on a modified Cummins L-10 engine with natural gas, it was observed that as the hydrogen additive was increased from 0 to about 20 vol% (7% by energy content) the NOx emissions steadily decreased by about 43% due to the ability to operate the engine more fuel lean and also with less spark advance while maintaining the non-methane hydrocarbons emissions constant. Increasing hydrogen content above 20 vol% caused the NOx to increase after adjusting the engine to maintain the same hydrocarbon emissions as the baseline. A 43% NOx reduction with a 7% by energy content hydrogen addition represents a leverage factor of greater than 6. Similarly in tests with gasoline (stoichiometric) engines with three-way catalysts indicated that hydrogen addition to natural gas dramatically reduced CO but increased NOx. However by tuning the engine to operate slightly richer than the baseline operating conditions, it was seen that some of this CO advantage could be sacrificed for significantly lower NOx emissions. Thus tests done in Denver demonstrated that it is possible to operate with Hythane containing 15 vol% hydrogen (5% by energy content) and reduce both CO and NOx to about 50% of the baseline values.

A cost analysis for a 500 vehicle fleet operating on Hythane (5% hydrogen by energy content) based on current liquid hydrogen pricing indicated that Hythane price would be quite competitive with regular unleaded gasoline at about \$1.13 per gallon gasoline equivalent<sup>2</sup>.

# **Hydrogen IC Engines**

A further enhancement of emissions reduction can be obtained by burning pure hydrogen in IC engines. As stated previously, this has been the subject of detailed investigation by Mercedes-Benz and BMW for quite some time. The approach is to use hydrogen in lean burn engines. Since the lean burn limit of air breathing hydrogen engines is so much greater than hydrocarbon fuels, it is possible to operate at very lean conditions and reduce NOx emissions to extremely low values. This is often accompanied by very low levels of CO emissions emanating from the combustion of traces of lubricating oils used in the engines. In the U.S. a demonstration program lead by Clean Air Now and Xerox Corporation operates a fleet of four service vehicles on hydrogen generated from solar energy at a fuel station in Los Angeles. A similar effort is underway in University of California's Riverside campus.

An improvement on this concept is the hydrogen hybrid electric vehicle which takes advantage of high efficiency electric drive trains and the low emissions of hydrogen IC engines. The concept involves the use of relatively small IC engines operating on hydrogen to power electric generators that charge batteries. The IC engine is sized to match the average power requirement of the vehicle and hence operates continuously at or near its optimum efficiency. The battery is sized to accommodate the peak power surge requirements. This reduces the weight of batteries needed for a given range and gives the vehicle rapid fueling capability. The hybrid electric vehicle is being actively developed for both hydrocarbon fuels and hydrogen. A hydrogen hybrid electric bus is currently undergoing testing in Atlanta by the Westinghouse Savannah River Company. This bus is slated to be put in transit service in Augusta, Georgia following this test program.

### Hydrogen Fuel Cell Vehicles

Perhaps the most attractive energy conversion technology that uses hydrogen in a zero-emission vehicle is the fuel cell. Although fuel cells were first invented some 150 years ago, only recently has their pace of development accelerated dramatically. Major automobile manufacturers in the U.S., Europe and Japan all have major development programs underway in an attempt to bring this technology to the market early in the next century. In the U.S. the joint program between the federal government and the "big three" auto manufacturers is actively developing fuel cell cars under the Partnership for a New Generation of Vehicles (PNGV) program.

While fuel cell cars are still under development, hydrogen fuel cell buses are becoming a reality and small fleets (3-4 buses at each location) will begin operation in Chicago, and Vancouver, British Columbia in 1997. The Canadian company Ballard Power Systems has developed the propulsion systems for these buses using their Proton Exchange Membrane (PEM) fuel cell technology. Hydrogen refueling stations at the bus depots are being built to deliver and store hydrogen onboard the buses at 3,600 psi. The hydrogen will be delivered to these sites as liquid and pumped to high pressures using cryogenic liquid pumps. The stations are being designed for fueling a bus in about 15 minutes.

## **Hydrogen Fuel Supply**

In the future, a truly zero emission transportation system could be based on hydrogen produced from renewable energy resources such as solar, wind, geothermal or biomass. However, renewable hydrogen production processes are still in the early stages of development and can not compete with current hydrogen production technologies. As the various hydrogen vehicle technologies rapidly progress towards commercialization, the ready availability of competitively priced hydrogen will be critical to their near term success. The perceived lack of a hydrogen fuel supply infrastructure could be the major barrier to the use of hydrogen in the transportation sector. Some major automobile companies such as Chrysler, Daimler-Benz, General Motors, and Toyota have decided to develop onboard fuel processors to generate the hydrogen required for their fuel cell vehicles from methanol or gasoline. However, it is entirely feasible to ensure an adequate hydrogen fuel supply system, at all stages of the evolution of hydrogen utilization technology, by adapting current industrial hydrogen production and distribution technologies.

About 40 million tons of hydrogen are commercially produced and consumed per year around the world. The energy content of this hydrogen is about 5 quadrillion British Thermal Units (BTU) or slightly more than 1 percent of the world's energy demand. About 95% of the 10 million tons per year of hydrogen produced in the U.S. is consumed "captively" within the producing facility to refine oil, or to produce ammonia and methanol. The rest is produced by a few industrial gas companies, and supplied to customers as a gas in high pressure cylinders and via pipelines, or as a liquid via over-the-road cryogenic tankers. This so called "merchant" hydrogen is used to manufacture specialty chemicals; to hydrogenate fats and oils; for reducing atmospheres in the manufacture of metals, glass and semiconductors; and as a coolant for large electric power generators. The only significant transportation fuel application of hydrogen - about 0.1% of the production - is as a rocket fuel, e.g., to launch NASA's Space Shuttle.

Practically all hydrogen is manufactured today, directly or indirectly, from fossil fuels. The most common commercially practiced technologies include: steam reforming of light hydrocarbons, partial oxidation of heavy oil, recovery from off-gases from the chlor-alkali industry, and refining and petrochemical processes, electrolysis of water, and methanol reformation.

The merchant hydrogen business in the U.S. is supported by well developed transportation and storage systems. Hydrogen is transported and stored as a gas, or liquid depending upon the distance from the user's location to the production plant, and usage rates and patterns, i.e., whether continuous or intermittent. Practically all commercial applications require the hydrogen in gaseous form, thus even when hydrogen is delivered and stored as liquid, it is vaporized at the customer's site prior to use. "Bulk" gaseous hydrogen is usually more expensive to store and ship than an equivalent amount of liquid hydrogen, particularly for distances greater than about 100 miles from the hydrogen production plant.

Among the various options being considered for storing hydrogen on-board the vehicle, perhaps the most challenging, from a fueling system design viewpoint, is high pressure gas at about 3,600 - 5,000 psi. The desired refueling times of about 10-15 minutes can be readily achieved with modifications to current commercial high pressure liquid hydrogen pumping systems. Fleets of up to 100 transit buses or 4,500 personal automobiles can be readily supported with liquid hydrogen deliveries and transferred at high pressure to the on-board tanks using special liquid hydrogen pumps followed by vaporization. Several high pressure hydrogen fueling systems for experimental fleets are currently being developed based on the significant experience gained in the design and operation of compressed natural gas fueling systems. The National Hydrogen Association is leading an effort to develop industry codes and standards for high pressure hydrogen fueling stations and onboard storage systems.

## Hydrogen Infrastructure Options To Support Fuel Cell Vehicles

A recently completed study<sup>3</sup>, examined how current commercial hydrogen production and supply technologies could be adapted to supply fleets of fuel cell cars at individual fueling stations and the economics of these options. Each car required 12 lbs. hydrogen stored onboard the vehicle as a gas at 5,000 psi. A typical fuel station was designed to dispense 3 tons per day (TPD) of hydrogen, sufficient to refuel 500 cars per day.

The following commercial options for hydrogen supply to the station were considered:

- Hydrogen produced from natural gas in large scale remote steam reformer plants (30-300 TPD), is delivered as liquid up to a distance of 500 miles from the plant.
- Hydrogen produced from natural gas in large regional steam reformer plants (30-300 TPD) is
  delivered via gas pipelines within a radius of 30 miles of the plant. Fueling stations are spaced 3
  miles apart on the pipeline.
- Hydrogen is produced at the fuel station with a dedicated on-site plant (3 TPD) using natural gas steam reformer, heavy oil partial oxidation, or a methanol reformer.

Table 1 summarizes the results of this study and shows the capital investment, and hydrogen price at the pump (without taxes) for these options. Hydrogen fuel can be supplied to the vehicle using current technologies at a cost ranging from \$1-2 per lb. depending on the scale of production. Taking into account the projection of a 2 to 3 times superior fuel economy of a fuel cell car over a gasoline car, the last column of Table 1 shows the maximum allowable gasoline price (without taxes) to provide the same cost per mile in an IC engine car as the fuel cell car. To compare this to a typical pump price for gasoline in the U.S., about 40¢ per gal should be added to these prices. With current regular unleaded grade gasoline prices at the pump in the U.S. at around \$1.20 per gallon, this analysis indicates that several near term hydrogen production and distribution options are close to being competitive with gasoline on a cost per mile basis.

Development of a hydrogen fuel infrastructure similar to the familiar gasoline supply network, with fuel stations every few miles, in population centers across the U.S. is certainly many years into the future. Large investment in the production and distribution infrastructure are necessary to achieve the lower prices for hydrogen. This certainly dictates that such facilities will not be built until sufficient demand for hydrogen develops as hydrogen-fueled vehicle technology becomes well established and accepted by the public. Thus, the infrastructure to supply fuel cell vehicles with hydrogen will evolve with the start up and growth of this market in several stages:

In regions where merchant hydrogen infrastructure exists, when a local market starts up with a small fleet of fuel cell cars, it would first be supplied by the current commercial distribution system via hauled-in high pressure gaseous hydrogen in tube trailers (to fuel about 20 cars per day) or liquid hydrogen (to fuel 20 - 500 cars per day). As the fleet grows large enough to support the continuous operation of a small reformer, one would be built and liquid hydrogen from a large central plant used as a backup source, and to meet peak demands. As the market grows even larger it could be supplied by a large regional reformer via pipeline, with the excess capacity being liquefied for distribution to areas remote from pipelines.

ľ

In areas where merchant hydrogen is not readily available small on-site hydrogen plants would be built to support the fuel station. Recent activity in the area of small reformers for hydrogen production may result in the economic size of on-site plants being reduced from currently accepted sizes. In this connection, methanol reformers appear to offer significant advantage due to their relative simplicity and wide availability of methanol.

Natural gas supplies would probably be sufficient to supply feedstock for hydrogen production for up to several million fuel cell cars, for several decades<sup>4</sup>. In the longer term, other renewable hydrogen production methods such as biomass gasification, or solar energy could be phased in.

### References

- Raman V., Hansel J., Fulton J., Lynch F. and Bruderly D., "Hythane An Ultraclean Transportation Fuel", Hydrogen Energy Progress X, Proceedings of the 10th World Hydrogen Energy Conference, Cocoa Beach, Florida, Vol. 3, p. 1797 (1994)
- Hansel J., Kielian D., Lynch F., Ragazzi R., Raman V., and Willson B, "Hythane A Status Report", 26th International Symposium on Automotive Technology and Automation, Aachen, Germany September 1993.
- Moore, R. B. and V. Raman "Hydrogen Infrastructure for Fuel Cell Transportation", presented at the 7th Annual U.S. Hydrogen Meeting, National Hydrogen Association, Alexandria, VA, April 1996.
- Ogden, J.M. et.al. "Hydrogen System Studies", presented at the U.S. DOE Hydrogen Program Review Meeting, April 29 - May 3, 1996.

Table 1. Cost Analysis for Hydrogen Infrastructure to Supply Fuel Cell
Automobiles

Hydrogen Production/Delivery Method	Size, TPD	Investment \$ Million	<u>Hydrogen</u> <u>Price</u> \$/lb	Untaxed Gasoline Equiv. Cost \$/gallon1
Remote Natural Gas Steam Reformer w/ Liquefier	30	63	1.52	1.12 - 1.61
	300	259	1.07	0.79 - 1.14
Regional Natural Gas Steam Reformer w/30 mile Gas Pipeline	30	82	1.32	0.97 - 1.39
	300	667	1.12	0.83 - 1.19
On-site Natural Gas Steam Reformer	3	9.6	1.62	1.19 - 1.71
On-site Partial Oxidation of Oil	3	12.5	1.80	1.33 - 1.91
On-site Methanol Reformation	3	6.8	1.70	1.25 - 1.80

<sup>&</sup>lt;sup>1</sup> Untaxed gasoline price to produce same cost per mile in IC engine vehicle as hydrogen in a fuel cell vehicle. The price range indicates different values for fuel economy based on two variants of the Federal Urban Driving cycle.